



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : <b>C08G 59/68</b>	<b>A1</b>	(11) International Publication Number: <b>WO 00/08087</b> (43) International Publication Date: 17 February 2000 (17.02.00)
<p>(21) International Application Number: PCT/EP99/05673</p> <p>(22) International Filing Date: 5 August 1999 (05.08.99)</p> <p>(30) Priority Data: P 9801693 6 August 1998 (06.08.98) ES</p> <p>(71) Applicant (for all designated States except US): UNIVERSITAT ROVIRA I VIRGILI [ES/ES]; Avyda. Paisos Catalans, E-43007 Tarragona (ES).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): CADIZ DELEITO, Virginia [ES/ES]; Universitat Rovira i Virgili, Avyda. Paisos Catalans, E-43007 Tarragona (ES). GALIA CLUA, Marina [ES/ES]; Universitat Rovira i Virgili, Avyda. Paisos Catalans, E-43007 Tarragona (ES). MANTECON ARRANZ, Ana [ES/ES]; Universitat Rovira i Virgili, Avyda. Paisos Catalans, E-43007 Tarragona (ES). REINA LOZANO, Jose Antonio [ES/ES]; Universitat Rovira i Virgili, Avyda. Paisos Catalans, E-43007 Tarragona (ES). RONDA BARGALLO, Juan Carlos [ES/ES]; Universitat Rovira i Virgili, Avyda. Paisos Catalans, E-43007 Tarragona (ES). SERRA I ALBET, Angels [ES/ES]; Universitat Rovira i Virgili, Avyda. Paisos Catalans, E-43007 Tarragona (ES).</p>	<p>(74) Agent: TÜRK GILLE HRABAL; Brucknerstrasse 20, D-40593 Düsseldorf (DE).</p> <p>(81) Designated States: AL, AU, BA, BG, BR, CA, CN, CZ, EE, HU, ID, JP, KR, LT, LV, MX, NO, PL, RO, RU, SG, SI, SK, TR, UA, US, YU, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p><b>Published</b> With international search report.</p>	
(54) Title: COMPOSITION OF CROSSLINKABLE EPOXY RESINS		
(57) Abstract		
<p>A composition of crosslinkable epoxy resin systems, comprising: A) one or more epoxy resins; B) one or more lanthanide triflates, the general formula of which is: <math>M(OSO_2CF_3)_{n-z}X_z</math>; where M is the cation derived from a Lanthanide, and n is the valence of the lanthanide in the compound, X is an additional organic or inorganic anionic residue, z is a number smaller than n or 0; C) optionally one or more crosslinking agents for epoxy resins; D) optionally pigments, fillers; and E) optionally other additives.</p> <div style="text-align: right; margin-top: 200px;"> <p>p. 4 epoxydohex</p> <p>p. 5 y triflate</p> <p>p. 9 Ex. 4</p> <p>p. 8 coating</p> </div>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## COMPOSITION OF CROSSLINKABLE EPOXY RESINS

### 5 SCOPE OF THE INVENTION

In general, this invention is related to compositions based on epoxy resins and, in particular, to the use of lanthanide triflates as curing agents for epoxy resin crosslinking and as accelerators in conventional curing processes of epoxy resins.

### 10 BACKGROUND TO THE INVENTION

Epoxy resins are substances that contain epoxide groups which can be crosslinked by catalysts and curing agents, leading to polymers with high mechanical and thermal resistance. These resins are used as adhesives, in coatings, in the manufacture of  
15 laminates and in a wide variety of applications that require high performance materials.

An epoxy resin can be cured using Lewis acids such as aluminium trichloride, boron trifluoride, iron trichloride and titanium tetrachloride. The Lewis acid catalyst co-ordinates with the epoxide oxygen and finally forms ether bonds through a cationic  
20 mechanism. Unlike other curing agents, such as primary amines, tertiary amines, polyfunctional amines or acid anhydrides, Lewis acids can catalyse the crosslinking of both glycidyl resins and cycloaliphatic epoxy resins and are active in a wide range of low concentrations. Epoxy resins with high contents of hydroxyl groups normally have high percentages of water which means that when they are crosslinked with Lewis acids the  
25 epoxide groups can be hydrolysed. So they are consumed in side reactions and the crosslinking is reduced considerably.

Because of the speed at which a Lewis acid cures an epoxy resin, the catalyst must be blocked, if storage of the coating composition is required. So, the blocked catalysts either  
30 do not react or only react slightly at room temperature, and require high temperatures to

start the reaction. Using this procedure longer "pot-life" times are achieved. An example of this catalyst is the use of complexes of boron trifluoride with ethers or amines as blocking agent. These initiators require a proportion of about three parts per hundred of resin (phr) and relatively high curing temperatures.

5 The most frequently used cationic catalysts in epoxy resin technology are boron trifluoride/amine compounds. Epoxy resin compositions catalysed by the compounds are relatively stable at room temperature and cure rapidly when they are exposed to high temperatures. However, these blocked catalysts have the disadvantage that not only the  
10 amine complexes are hygroscopic and hydrolyse with moist air, but additionally the physical and electrical properties of the resin will deteriorate at high temperatures and at high levels of moisture.

So there is a need for new cationic catalysts which are suitable for epoxy resin technology  
15 and which overcome the drawbacks of the catalysts used previously.

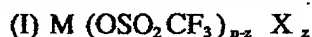
#### SUMMARY OF THE INVENTION

This invention provides a solution to the need of better crosslinking agents and  
20 accelerators for epoxy resin systems, using lanthanide triflates (trifluoromethanesulphonates) for epoxy resin and modified epoxy systems, preferably used for coating systems. The lanthanide triflates act as blocked catalysts and have various advantages. They are tolerant to water, stable at room temperature and highly soluble in organic compounds. The solubility or dispersability of the crosslinking or  
25 curing agent in the epoxy resin is an important advantage because normal heterogeneous dispersions cluster together during storage and show less reactivity. These catalysts also need to be soluble in the epoxy resin for the manufacture of prepegs. Additionally, the toxicity of lanthanide salts is much lower than the toxicity of other transition metals and similar to that of alkaline metals, which provides advantages in handling of this substances.

## DETAILED DESCRIPTION OF THE INVENTION

This invention provides a composition of crosslinkable epoxy resin materials, referred to below as the composition of the invention, comprising:

- 5 A) one or more epoxy resins  
B) one or more lanthanide triflates, the general formula of which is



where

M is the cation derived from a Lanthanide, and

10 n is the valence of the lanthanide in the compound,

X is an additional organic or inorganic salt residue (anionic residue),

z is a number lower than n or 0;

- 15 C) optionally one or more crosslinking agents for epoxy resins  
D) optionally pigments, fillers and  
E) optionally other usual additives

20 The composition of the invention can be liquid or solid. The composition of the invention may comprise the components A and B or it may comprise components A, B and C and optionally components D and E may be included. One preferred embodiment of the invention is a composition which is suitable for powder coating applications. However, the compositions are also useful in liquid coating agents. Another embodiment of the invention is the process of crosslinking compositions comprising components A and  
25 optionally components C, D and E by incorporation of lanthanide triflates (I) in the composition

30 In the sense used in this description, the term "epoxy resin" as component A includes any monomeric, dimeric, oligomeric or polymeric epoxy material which contains one or more functional epoxy groups, either liquid or solid. As an example, component A may be:

- an epoxy resin which is the result of the reaction of Bisphenol A [2,2-bis (4-hydroxyphenyl) propane] and the epichlorohydrine [1-chloro-2,3-epoxypropane];
- an epoxy resin which is the result of the reaction between phenolformaldehyde resins of low molecular weight and epichlorohydrin; whereby these resins can be used by themselves or in combination with additional compounds such as phenylglycidylether, glycidyl acrylate, glycidyl methacrylate, styrene oxide, allyl glycidylether, etc., as reactive diluent, which can be used to modify the viscosity of the resin;
- polymers which contain terminal, lateral or internal epoxide groups, e.g. the vinyl copolymers which contain glycidyl acrylate or methacrylate as comonomer or polymers which incorporate cycloaliphatic epoxide group containing monomers;
- modified epoxy resins, which generally have epoxide functional groups at the end or lateral of their chains, such as epoxy siloxane, epoxy polyurethane, epoxy polyester, epoxy polyether, epoxy polyamine, etc. and
- epoxy resins modified with carboxylic acids, alcohols, amines, phenols, thiols, etc. as long as they contain at least one or more reactive epoxide group per molecule.

For a review of suitable epoxy resins and methods for the manufacture see, for example, *Epoxy Resins. Chemistry and Technology*, 2nd Edition, Ed. C. A. May, Marcel Dekker, New York (1988); *Handbook of Epoxy Resins*, H. Lee and K. Neville, Ed. McGraw Hill (1982), or *Chemistry and Technology of Epoxy Resins*, B. Ellis (Editor), Ed. Blackie Academic and Professional (1994), which are included by reference herein.

Preferably the component A is selected from the group made up of Bisphenol A diglycidyl ether resin (DGEBA), 3,4-epoxycyclohexylmethyl resin, 3,4-epoxy-cyclohexanocarboxylate resin and dodecylen-N,N'-bis (epoxynadimide) resin. Component A may consist of one epoxy resin or a mixture of different types of epoxy resins can be used. The mixture can be selected according to the desired properties of the composition, e.g. viscosity, reactivity, crosslinked network.

Component B is a lanthanide triflate of formula (I) described above. In the meaning used in this description, the term lanthanide (M) shall be selected out of lanthanum and each of the chemical elements whose atomic number is between 58 (cerium) and 71 (lutetium), inclusive. In general, all lanthanides function in a similar fashion, but due to their different cationic structure they lead to crosslinked products which are different in the amount of crosslinking and glass transition temperature (T<sub>g</sub>) and which influence also the reaction conditions. In one particular embodiment of this invention, the lanthanide is selected from the group made up of lanthan, ytterbium and samarium.

Some lanthanide triflates (I) are commercial products or can be obtained by conventional, well-known methods [see, for example, M. EL. M. Hamidi, M. Hnach and H. Zineddine, J. Chim. Phys. (1997), 94, 1295-1303]. As X other organic and/or inorganic salt residues can be used, e.g. anions such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>PO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, C<sub>2</sub>H<sub>5</sub>OO<sup>-</sup>, C<sub>6</sub>H<sub>5</sub>COO<sup>-</sup> which may form mixed salts with the lanthanide M.

Z is a number between 0 and n - 1, so that at least one triflate residue is included in component (I). Preferably the component B consists of lanthanide triflates, wherein Z is 0 or 1, most preferably Z is 0. The organic or inorganic salt residues shall be selected in a way that they do not disturb the homogeneity of the mixture of components A, B and the optional components. The component B may comprise one metall ion M, but it is also possible to use a mixture of two and more different metall ions.

The component B can be present in the composition in a very wide range, but normally a range between 0.1 and 7 phr is preferred. The amount of component B may be varied to influence certain properties. When the proportion of the component B is about 0.2 phr the curing of the composition takes place at higher temperatures. If the amount of component B is about 5 phr the curing proceeds faster at lower temperature. According to the amount of compnent B specific properties of the coating composition can be adjusted according to the application purpose.

A composition of the invention can be prepared by mixing component A with an effective quantity of component B, the lanthanide triflate (I). Depending on the compatibility of the lanthanide triflate (I) and component A, component B can be mixed directly into component A or it may be dissolved or dispersed in an organic solvent such as methylene chloride, methanol, etc., which is useful for liquid coating materials to obtain a practically homogenous mixture. When component A is solid, the component B can be incorporated and mixed also by dry-grinding or by fusion mixing. Also small amounts of auxiliary solvents may be used for dissolving or dispersing component B to facilitate the mixing process of this component in the solid resins. Additionally this process may be performed by application of elevated temperature to soften or melt the component A and subsequent homogenisation.

As component C the composition of the invention may contain conventional crosslinking agents and substances, e.g. primary and tertiary amines, acid anhydrides, dicyandiamide(DICY) and its derivatives, imidazoles, imidazolines, ureas, amides, melamines, hydrazides, guanidines, thioureas and sulphonamides among other products which are habitually used in the curing of epoxy resins. The crosslinking agent is present in the suitable stoichiometric or non-stoichiometric ratio. This composition can be obtained by mixing appropriate amounts of the various components.

Another composition of the invention comprises at least one epoxy resin (A), a lanthanide triflate (B) and a conventional crosslinking agent (C) .

The ratio between component B and the components A and C can vary considerably.

However, good results are obtained when the quantity of component B used is between 0.2 and 5 phr of the total mixture. The mixing process for liquid or solid compositions of components A and C together with component B may be performed as described above, and as mentioned above it is preferred to obtain a homogenous dispersion or solution of the three components.

As component D the composition of the invention may, e.g. contain pigments, fillers ,



fibres and/or dyes. Pigments are well known in the paint industry, and are organic or inorganic pigments e.g. titanium dioxide, carbon black, chromium titanium yellow, ferroxide red, effect pigments like metallic pigment flakes or iriodine pigments or organic pigments like phthalocyanine, chinacridone or azopigments. As fillers e.g. barium sulphate, calcium sulfates, siliciumdioxide and /or kaolin may be used. For specific purposes additonally fibres may be incorporated. The component D shall be stable at the curing temperature e.g. up to 200 °C. For use as powder coating material, however also as liquid coating material, the composition of the invention shall preferably contain colouring pigments and fillers.

As component E other additives may be incorporated in the composition of the invention. Examples of such components are surfactants, catalysts, matting agents, solvents, accelerators, plasticisers, agents for controlling viscosity, UV protectors, reinforcing agents, etc., which are well known to a skilled person and which may be selected according to the different field of use of the composition. For liquid compositions solvents, reactive solvents, and other liquid additives may be used. For use in powder coating materials preferably solid additives shall be used as component E.

The mixing process of the composition is known in principle, liquid materials may be dissolved or dispersed and then mixed, solid components may be mixed after heating and melting or they may be mixed by dry grinding. If necessary the pigments or fillers may be ground to an appropriate particle size. Such manufacturing process may be selected according to the specific composition of the invention and the purpose of use of this material; such processes are known to a skilled person. For all operations it is necessary to keep the temperature below the start of a crosslinking reaction of the components.

The composition of the invention can be crosslinked by heating it to a temperature between 90 and 250 °C for between 0,5 and 90 minutes. Preferably the temperature shall be between 100 and 200 °C and the period may vary between 1 to 60 minutes. In general, an increase in the amount of component B leads to lower curing temperatures.

Lanthanide triflates can be used according to the invention as catalyst or accelerator for epoxy resin systems and they do not have the well-known disadvantages of other catalysts or accelerators which are normally used in epoxy resin technology and which are discussed in the prior art.

5

Using lanthanide triflates (I) as component B as accelerating agents in epoxy resin systems for curing epoxy resins (component A) optionally together with crosslinking agents (component C) saves a considerable amount of energy since it shortens the time required for the curing and reduces the temperature at which the curing takes place.

10

Additionally, such compositions according to the invention have the advantage that their use results to lower heat evolved during the crosslinking reaction, which is advantageous for curing objects of large dimensions or large quantities of materials in reducing the problem of dissipating the heat produced during curing. In this case, however, the curing takes place at unexpectedly short curing times compared with smaller volumes of such materials.

15

Another advantage of the use of component B is that in other numerous formulations comparable reaction processes require catalysts, the residues of which lead after the curing to problems of oxidation, premature ageing of the materials, yellowing, etc. which can be avoided by the invention.

20

The composition of the invention can be used in any application of epoxy resins, with or without a crosslinker, for example as liquid coating or as solid coating material, as adhesive, in the manufacture of laminates or composites and in other applications.

25

The following examples illustrate particular ways of using the invention.

## Example 1

A crosslinking composition of epoxy resins was prepared by mixing 0.5 g of a Bisphenol A diglycidyl ether resin (DGEBA) of a molecular weight of 348 with 5 mg (1 phr) of ytterbium triflate and dissolving both in a minimum quantity of methanol with the aim of achieving a homogeneous mixture. The methanol was eliminated under vacuum. The mixture was heated to 130 °C for 35 minutes, and the curing was total and produced a crosslinked epoxy resin with a glass transition temperature of 97 °C.

## Example 2

A curing mixture was prepared by dissolving 0.5g of DGEBA of a molecular weight of 348 and 5mg (1 phr) of samarium triflate in the minimum quantity of methanol. The mixture was evaporated to dryness and was then heated at 150 °C for 35 minutes. The resulting crosslinked resin had a glass transition temperature of 88 °C.

## Example 3

The procedure in Example 2 was repeated but with 1 phr of lanthanum triflate. The material was totally cured by heating the evaporated mixture at 150 °C for 30 minutes. It had a glass transition temperature of 84 °C.

## Example 4

A homogeneous mixture was made of 0.5 g of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate and 5 mg (1 phr) of ytterbium triflate dissolved in a minimum quantity of methanol and dried under vacuum. After heating for 30 minutes at 120 °C, the product was totally crosslinked.

## Example 5

A homogeneous mixture was made of 0.5 g of dodecylen-N,N'-bis (epoxynad-imide) and 10 mg (2 phr) of ytterbium triflate. By heating the mixture at 150 °C for 30 minutes the material becomes crosslinked and has a glass transition temperature of 76 °C.

## Example 6

A homogeneous mixture was made of 0.1 g of DGEBA with a molecular weight of 348 and 0.043 g of tetrahydrophthalic anhydride and 1.4 mg (1 phr) of ytterbium triflate by dissolving it in the minimum quantity of methylene chloride and methanol and drying under vacuum. A dynamic scan of this mixture in a differential scanning calorimeter (DSC) showed a curing exothermic between 100 and 200 °C with its maximum temperature at 170 °C. The resulting product is totally crosslinked even though this technique does not show the glass transition temperature.

Differential calorimetry shows no reaction exotherm below 260 °C when the same experiment is carried out without ytterbium triflate. The product which results from this experiment is soluble in organic solvents which demonstrates that curing has not taken place.

## Example 7

Two homogeneous mixtures were made of 0.1 g of DGEBA with a molecular weight of 348 and 0.01 g (10 phr) of N,N-dimethylaminopyridine (DMAP). Ytterbium triflate (0.5 mg) (0.5 phr) was added to only one of them. A dynamic scan of both mixtures in a differential scanning calorimeter (DSC) showed curing exothermic in both experiments. The sample that contained 0.5 phr of ytterbium triflate had the exotherm peak some 20 °C below the sample that did not contain it. The resulting products were totally crosslinked, although this technique did not allow the glass transition temperatures to be evaluated.

## Example 8

Two homogeneous mixtures were made of 0.1 g of DGEBA with a molecular weight of 348 and 0.01 g (10 phr) of 2-methylimidazol. Ytterbium triflate (0.5 mg) (0.5 phr) was added to only one of them. A dynamic scan of both mixtures in a differential scanning calorimeter (DSC) showed, as in Example 7, that the curing exothermic had shifted to lower temperatures for the sample that contained the ytterbium triflate.

The resulting products proved to be insoluble and the glass transition temperatures were both about 107 °C.

#### Example 9

5 Two homogeneous mixtures were made of 0.2 g of DGEBA with a molecular weight of 348 and 7 mg of dicyandiamide (DICY) (7:1 mol epoxide/moles DICY). One milligram (0.5 phr) of ytterbium triflate was added to only one of them. A dynamic scan of both mixtures in a differential scanning calorimeter (DSC) showed curing exothermic in both experiments. The sample that contained 0.5 phr of ytterbium triflate had the exotherm  
10 peak some 20 °C below the sample that did not contain it. The resulting products were totally crosslinked, although this technique did not allow the glass transition temperatures to be evaluated.

#### Example 10

15 Two homogeneous mixtures were made of 0.2 g of DGEBA with a molecular weight of 1.250 and 2 mg (1 phr) of curing agent. In one of them the agent was boron trifluoride /monoethylamine and in the other it was ytterbium triflate. Differential scanning calorimetry (DSC) showed that after 30 minutes both mixtures were totally cured, being heated at 190 °C. The resulting products were totally crosslinked and the mixtures  
20 catalysed with boron and ytterbium triflate had glass transition temperatures of 77 °C and 107 °C, respectively. This indicates that, being the chemical structure of both networks similar, the degree of curing is higher for ytterbium triflate. This example reveals that by using different curing agents [boron trifluoride /monoethylamine (traditional) and ytterbium triflate (invention)] in the same ratio and in similar curing conditions, the  
25 degree of crosslinking is higher when the curing agent is ytterbium triflate as it can be inferred from Tg values and measured reaction enthalpies.

#### Example 11

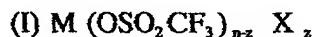
30 Two homogeneous mixtures were made of 0.25 g of 3,4-epoxy cyclohexylmethyl-3,4-epoxycyclohexane carboxylate and 0.1 g of diaminodiphenylether. To one of these

5 mixtures 2.5 mg (1 phr) of ytterbium triflate were added, dissolved in a minimum quantity of methanol and dried under vacuum. A dynamic scan of this mixture in a differential scanning calorimeter (DSC) showed a curing exotherm with a maximum at 132 °C. The resulting product was totally crosslinked, although this technique did not reveal the glass transition temperature.

10 The same experiment was carried out without the ytterbium triflate and differential calorimetry showed no reaction exotherm below 260 °C. The product which resulted from this experiment was soluble in organic solvents which demonstrated that the curing had not taken place.

## CLAIMS

- 5 1. A composition of crosslinkable epoxy resin systems, comprising  
A) one or more epoxy resins,  
B) one or more lanthanide triflates, the general formula of which is



where

- 10 M is the cation derived from a Lanthanide, and  
n is the valence of the lanthanide in the compound,  
X is an additional organic or inorganic anionic residue,  
z is a number smaller than n or 0;  
C) optionally one or more crosslinking agents for epoxy resins  
15 D) optionally pigments, fillers and  
E) optionally other additives.

2. Composition according to claim 1, wherein said epoxy resins are a mono-  
meric, dimeric, oligomeric or polymeric epoxy material containing one or more epoxy  
20 functional groups.

3. Composition according to claim 1 or 2, wherein said epoxy resins are  
polymers containing two or more terminal, lateral or internal epoxy groups.

- 25 4. Composition according to claims 1 to 3, wherein said epoxy resins are  
modified epoxy resins, selected from siloxane epoxy resins, polyurethane epoxy resins,  
polyester epoxy resins and polyamine epoxy resins containing epoxy functional groups.

5. Composition according to claims 1 to 3, wherein said epoxy resin is a  
30 reaction product of Bisphenol A and epichlorohydrin.

6. Composition according to claims 1 to 5, wherein the composition includes a crosslinking agent (component C), selected from the group consisting of amines, anhydrides, dicyandiamide, imidazoles, imidazolines, ureas, amides, melamines, hydrazides, guanidines, thioureas and sulfonamides and its derivatives.

5

7. Composition according to claim 6, wherein the composition includes additionally pigments and/or fillers (component D).

10

8. Composition according to claims 1 to 7, wherein the composition is liquid and includes solvents and/or other additives (component E).

9. Composition according to claims 1 to 7, wherein the composition is solid and contains other additives (component E).

15

10. Composition according to claims 1 to 9, wherein the lanthanide triflates (I) of component B are selected from the group consisting of triflates of lanthanum and the chemical elements with atomic number between 58 and 71, both included.

20

11. Composition according to claim 10, wherein said lanthanide triflates (I) are selected from the group consisting of lanthanum, ytterbium and samarium triflates.

12. Composition according to claims 10 and 11, wherein component B contains only one species of metal ion.

25

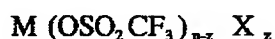
13. Composition according to claim 10 to 12, wherein the number of other salt residues Z is 0 or 1, preferably 0.

30

14. Composition according to claims 1 and 10 to 13, wherein said component B is present in an amount varying from 0.1 and 7 parts by weight per 100 parts by weight of component A and C preferably from 0.2 and 5 parts per 100 parts.



15. A process for crosslinking a composition of one or more epoxy resins, optionally one or more crosslinking agents for epoxy resins, optionally pigments, fillers and other additives by incorporating one or more lanthanide triflates, the general formula of which is



where

M is the cation derived from a Lanthanide, and

n is the valence of the lanthanide in the compound,

X is another organic or inorganic salt residue,

z is a number smaller than n or 0;

in an amount of 0.2 to 5 phr in the composition.

16. A process for crosslinking a composition according to claim 15 wherein the lanthanide triflate is practically homogenously dissolved in the components A and C of the composition.

17. A process for crosslinking a composition according to any of claims 1 to 14, or obtainable through the process of claim 15 or 16, comprising heating this composition between 90 and 250 °C for a period of time between 1 and 60 minutes.

18. A powder coating composition, comprising a composition according to any of claims 1 to 14.

19. A liquid coating composition, comprising a composition according to any of claims 1 to 14.

20. A substrate coated with a coating composition containing a composition according to any of claims 1 to 14.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 99/05673

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08G59/68

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 842 019 A (KROPP) 15 October 1974 (1974-10-15) column 2, line 12 -column 3, line 6 column 5, line 59 -column 7, line 33; claims 1,2,7-9,16-18,21; example 5	1-3, 10-12
X	EP 0 493 916 A (CIBA-GEIGY) 8 July 1992 (1992-07-08) page 2, line 29 -page 5, line 49; claims 1,2; examples 6-9	1-3,5-12
A	EP 0 139 042 A (UNION CARBIDE ) 2 May 1985 (1985-05-02) page 20, line 5 -page 21, line 26; claim 17	1-3
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

12 November 1999

Date of mailing of the international search report

24/11/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Bourgonje, A

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/05673

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 475 069 A (DRYSDALE) 12 December 1995 (1995-12-12) column 2, line 4 - line 31 -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/05673

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3842019 A	15-10-1974	CA 953444 A	20-08-1974
		CH 552029 A	31-07-1974
		DE 2016018 A	15-10-1970
		FR 2042937 A	12-02-1971
		GB 1314561 A	26-04-1973
		JP 48023554 B	14-07-1973
EP 493916 A	08-07-1992	DE 69125131 D	17-04-1997
		DE 69125131 T	30-10-1997
		ES 2099142 T	16-05-1997
		JP 4314719 A	05-11-1992
		US 5362835 A	08-11-1994
EP 139042 A	02-05-1985	US 4707535 A	17-11-1987
		CA 1246591 A	13-12-1988
		US 4786705 A	22-11-1988
US 5475069 A	12-12-1995	NONE	